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An Improved Method to Increase the Concentration of Graphene in Organic Solvent

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We added an organic additive 2-amino-2-methyl-1-propanol (AMP) and water to dimethylformamide (DMF) and exfoliated graphite therein to prepare graphene. When the content of AMP was 1.0 vol % and the content of water was 0.4 vol %, the dispersion of graphene was obtained at the concentration up to 0.3 mg mL^{-1}, which was 50% higher than that obtained by directly exfoliating graphite in DMF for 24 h. At the same time, the graphene sheets maintained high quality with little impurity.

Graphene has exhibited unique properties[1,2] since it was discovered in 2004, and various devices based on graphene have been fabricated.[3] However, industrial applications are hampered by the low productivity of graphene. Sonication[4–7] is considered to be an efficient method to obtain large-scale production of graphene. Graphene can be obtained by sonicating graphite in water[5,6] or in organic solvent.[7] In water, since the graphene is hydrophobic, surfactants such as sodium cholate or 1-pyrene-butyrate have to be added to modify the surface of graphene or the graphite has to be oxidized beforehand. Although a stable dispersion of graphene is obtained, undesired impurities can be left on graphene sheets because of the surfactant's strong adsorption affinity for graphene surface via π–π stacking[8,9] or structure defects are formed during the oxidation.[10,11] High-quality graphene can be obtained by sonicating graphite in some organic solvents, but the concentration of graphene is usually very low, typically less than 0.01 mg mL^{-1}.[12] Some efforts have been made to increase the concentration of graphene in organic solvent. Khan et al.[13] tried low-power sonication in *N*-methylpyrrolidone for 460 h to obtain high concentration, up to 1.2 mg mL^{-1}. But the sonication time is too long to be practical. Herein, we report an efficient method to increase the concentration of graphene with high quality, few impurities, and shorter sonication time.

DMF/AMP (1.0 vol %) solution was prepared by adding 0.2 mL of AMP to 20 mL of DMF. In order to obtain high concentration of graphene, different amounts of deionized water were added to DMF/AMP solution. After stirring the solution for 10 min, 0.4 g of pristine graphite powder (spectrum purity) was added. Then the graphene dispersion was prepared by sonicating graphite in a water bath for 24 h at power outputs of 72 W. To prevent overheating of the sonicator and to keep the temperature of the solution constant, circulating water was used. After 24 h, the dispersions were centrifuged at 4000 rpm for 90 min to remove thick graphene sheets and unexfoliated graphite. And then, the supernatant liquid was carefully poured out and retained. The absorbance of graphene was measured using a UV–vis spectrometer at the wavelength of 660 nm, and the concentration of graphene was calculated according to the absorption coefficient.[13]

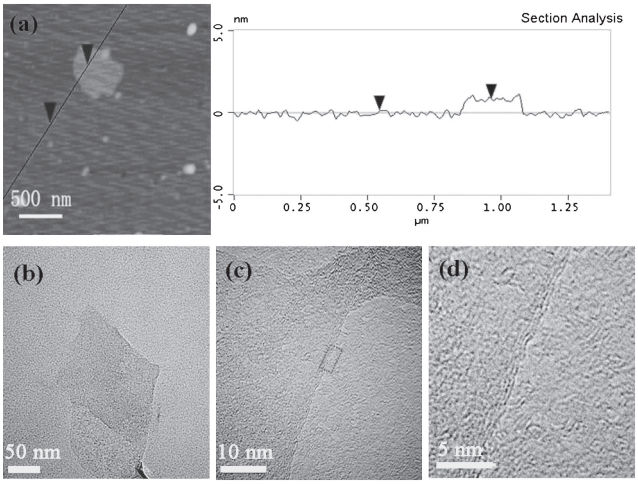


Figure 1. (a) AFM image of graphene sheet on mica substrate (left) and corresponding height profile (right); (b), (c) TEM images of graphene sheets, (d) a magnified version of the portion of (c) in the dashed box.

In Figure 1a, the as-prepared graphene-sheet-surface topography is clearly demonstrated. From AFM images, it can be observed that the clean graphene is obtained with few impurities on the surface. The height profile indicates that the graphene size is about 400 nm and that its thickness is 0.736 nm. It may be a double-layer graphene sheet as the single-layer graphene thickness is 0.335 nm. And from TEM images, triple-layer graphene is confirmed by counting the edges of graphene flakes, as shown in Figure 1d. From Figures 1a–1d, the graphene lateral size is estimated to be about 200–500 nm and the thickness is less than 5 layers.

Figure 2 shows that the concentration of graphene varies with the water content. As the water content increases, the concentration of graphene in DMF/AMP (1.0 vol %)/water solution increases as well. But it starts to decrease beyond 0.4 vol % water content. We obtain a dispersion of graphene in DMF/AMP/water solution at the concentration up to 0.3 mg mL^{-1}, when 0.4 vol % deionized water is added to the DMF/AMP (1.0 vol %) solution. Moreover, under the same sonication conditions, the concentration of graphene obtained by simply exfoliating graphite in DMF is 0.205 mg mL^{-1}. The increased concentration can be attributed to the appropriate contents of water. AMP is often used as efficient codispersant for pigment and contributes pH stability. It can be well dissolved in DMF and ionized. Therefore, the graphene sheets can be charged by adsorption on the surface of graphene, as illustrated in Scheme 1. We applied a constant electric field of 100 V cm^{-1} between a copper anode and a copper cathode which were immersed in the graphene dispersion, and we observed that

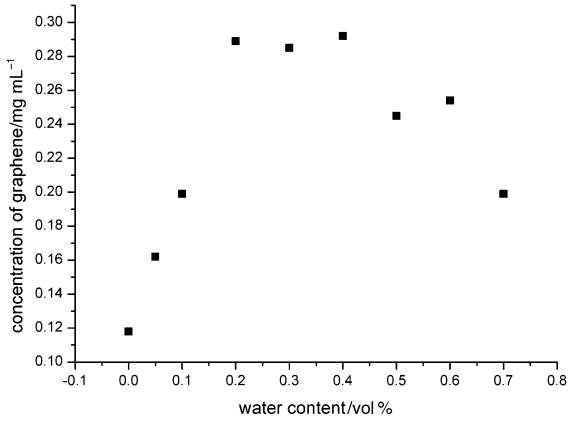
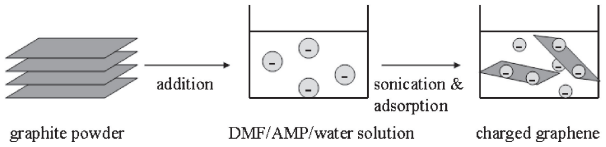


Figure 2. The effects of water content on the concentration of graphene dispersed in AMP (1.0 vol %)/DMF/water solution.



Scheme 1. Scheme for the charged graphene sheets through adsorption.

graphene sheets in the dispersion moved toward the anode in the electric field, and thus the graphene sheets are further testified to be negatively charged. In graphene colloid obtained by simply exfoliating graphite in DMF, the van der Waals force between graphene sheets is attractive, and thus the graphene sheets tend to restack when one graphene sheet collides with another. However, when the graphene is charged, a diffuse electric double layer may form around the graphene sheets and two similarly charged surfaces usually repel each other electrostatically to decrease the restacking tendency. The electrostatic repulsion allows more exfoliated graphene sheets to disperse, which results in an increased concentration. However, it should be noted that another factor, the surface energy of solution, can also influence the concentration of graphene.[12] As the AMP is added to DMF, the surface energy of the solution can be changed to mismatch that of graphene, resulting in low concentration as illustrated in Figure 2. Therefore, we added deionized water to facilitate the ionization of AMP to increase the electrostatic repulsion. However, with too high water content, since the surface energy of water mismatches that of graphene, it may lead the surface energy of solvent DMF/AMP/water to mismatch that of graphene. The balance of electrostatic repulsion and solution surface energy determines the concentration of graphene. From Figure 2, we can see that the best balance is achieved when 0.4 vol % deionized water is in DMF/AMP (1.0 vol %) solution. The obtained dispersion is so stable that the concentration is only decreased by 0.02 mg mL^{-1} after 1 month.

The Fourier transform infrared (FT-IR) spectra were employed to test whether the residual solvent or additive remains on the graphene sheets (Figure 3). We measured the FT-IR spectra of the graphite powder, the DMF/AMP/water solution, and the graphene powder obtained after drying at 90 °C. For DMF/AMP/water, the peak at 3538 cm^{-1} can be attributed to O–H stretching vibrations of water molecules, and the peaks at 2925 and 2858 cm^{-1} can be attributed to the C–H stretching vibration of methylene group in AMP. The presence of methyl groups is not detected at around 2962 and 2872 cm^{-1} because of the presence of stronger peaks of methylene groups nearby, but it can be detected at 1388 cm^{-1}. And the peak at 1093 cm^{-1} can be attributed to the C–N stretching vibration of the amino group. The presence of the amide group in DMF can be detected at around 1674 (C=O stretching vibration) and 1257 cm^{-1} (C–N stretching vibration). In the spectrum of graphene, the peaks at 3538, 2925, 1257, and 2858 cm^{-1} disappear, which indicates that water, AMP, and most of DMF have been removed. The peaks around 1674, 1506, and 1388 cm^{-1} are weak and blurred, indicating that an extremely low amount of DMF remains on graphene sheets. As for the broad peak at around 970 cm^{-1}, it belongs to none of the solvent peaks, so it may be an impurity introduced from elsewhere during preparing or testing sample. Compared with other surfactants, AMP can charge graphene sheets by physical adsorption and has higher volatility. Therefore, during the drying process, AMP can be readily removed from graphene sheets. It is very helpful to prepare pure graphene without undesired surfactants and the like.

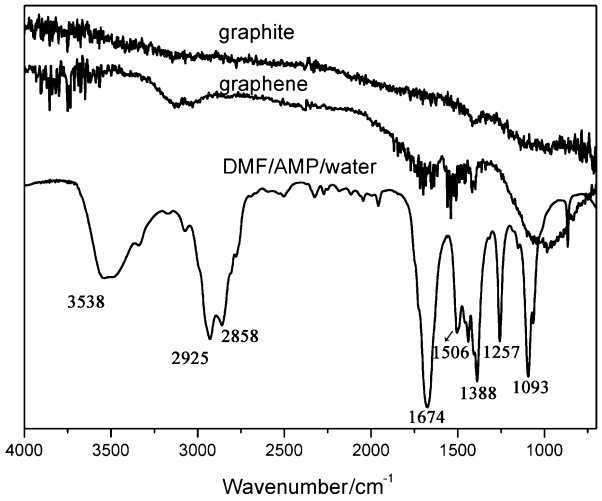


Figure 3. FT-IR spectra of graphite, graphene, and DMF/AMP/water solution.

Raman spectra were employed to further characterize the structure of graphene, including defects or disorders and graphene layer numbers. The graphene sample was prepared by depositing a layer of graphene on quartz. Since the graphene size is ca. 200–500 nm, much smaller than the size of Raman excitation beam (ca. 2 μm), a large quantity of graphene sheets can be examined by the beam. It is known that the D band (ca. 1350 cm^{-1}) is sensitive to the presence of defects or disorder in graphene,[14] while the 2D band (ca. 2700 cm^{-1}) is indicative of the graphene layer numbers.[15] In Figure 4, the presence of a D band may be induced by disorder. Since the graphene sheets have relatively small size and a large quantity of edges of graphene are examined, the edge-induced disorders of graphene sheets increase the intensity of the D band and result in the

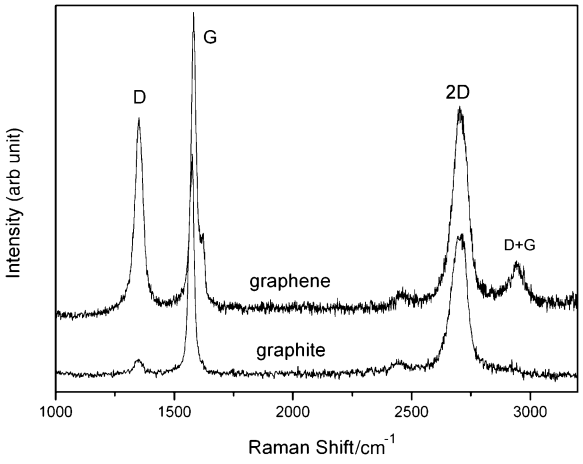


Figure 4. Raman spectra for graphene and graphite powder.

presence of D + G band (ca. 2942 cm^{-1}).[14] And this result is similar to observations reported.[13]

Reina et al.[16] have reported that the thickness of the graphene flakes is related to the intensity ratio of the 2D and G peaks, $I(2D)/I(G)$. As the thickness increases, $I(2D)/I(G)$ decreases monotonically from a high of 2.1 ± 0.2 for single-layer graphene to 0.8 ± 0.1 for quadruple-layer graphene. In our experiment, $I(2D)/I(G)$ was calculated to be 0.69, indicative of the graphene sheets thinner than 5 layers, which is consistent with the results of AFM and TEM.

In summary, we exfoliated graphite powder to prepare graphene dispersion in organic solvent DMF. When 1.0 vol % AMP and 0.4 vol % deionized water were added to DMF, the dispersion of graphene in DMF/AMP/water solution was obtained at the concentration up to 0.3 mg mL^{-1} after 24 h sonication, 50% higher than that obtained by simply exfoliating graphite in DMF. The reason for the increased concentration was studied, which may be attributed to additional electrostatic repulsion induced by AMP. Moreover, the graphene sheets were clean with few impurities or defects after drying at low temperature as shown in FT-IR and Raman spectra. The AFM and TEM show that the graphene sheets have the size of about 200–500 nm and thickness of less than 5 layers.

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